PATENT SPECIFICATION

NO DRAWINGS

1,163,023

Date of Application (No. 42858/66) and filing Complete Specification: 26 Sept., 1966.

Application made in Germany (No. W40009 IVc/12c) on 30 Sept., 1965.

Complete Specification Published: 4 Sept., 1969.

Index at acceptance:—B8 CA

International Classification:—B 01 j 13/00

COMPLETE SPECIFICATION

Encapsulation of Particulate Materials and Liquids

We, GUNTHER WAGNER PELIKAN-WERKE, 3 Hanover 1, Podbielskistrasse 141, Germany, a German Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention generally relates to encapsulation and is particularly directed to a method of producing capsules which envelop liquids and/or solid substances. The term "capsule" as used herein is deemed to refer to an envelope of film material in which the liquid and/or solid substance is completely encapsulated. The sizes of the capsules obtained by this invention generally have sizes between 0.001 and 2 mm.

Several procedures have previously been suggested for producing capsules of the indicated kind. According to one of the prior art proposals, the capsules are produced pursuant to the principle of coacervation. Pursuant to a different suggestion, the capsule formation and the enveloping of solid and/or liquid substances is accomplished by polycondensation.

All the prior art procedures, however, have serious drawbacks, are cubersome to carry out and render it difficult effectively to control the capsule formation, particularly as to size and thickness of the capsule wall.

Accordingly, it is a primary object of this invention to provide a method of producing capsules, which overcomes the prior art disadvantages and drawbacks and which results in the formation of capsules of the desired quality and size.

Another object of the invention is to provide a method of the indicated kind which is easy to carry out and to control and which does not require elaborate equipment.

According to this invention we provide a method of forming capsules, each capsule comprising an envelope of film material encapsulating a substance, the method comprising preparing a dispersion system by mixing:

(D) the substance to be encapsulated,

(B) a liquid dispersion medium, and

at least two components (A) and (C) capable of reacting chemically with each other to form film capsules around particles of the substances to be encapsulated, one of the said components (A) being selected from metal alginate, metal carrageenate, metal carboxymethyl-cellulose, cellulose xanthogenate, unsaturated polyester and cellulose esters, and the other components being a low molecular substance selected from metal salts having a multi-valent cation, organic acids, minerals acids, organic peroxides and *o*-titanic acid esters, whereby particles of the substance (D) are encapsulated by the film thus formed.

The inventive procedure of forming capsules generally comprises preparing a dispersion system, in which the dispersed phase is the substance (D) to be encapsulated and the continuous phase (B) is water or an organic solvent. At least two components (A) and (C) are necessary which are capable of reacting chemically with each other to form film capsules around the substance to be encapsulated.

(A) is a film-forming substance of high molecular weight and (C) is a substance of low molecular weight.

In order to make capsules one dissolves (A) in (B) and (C) in (D) and disperses the solution of (C) in (D) in the solution of (A) in (B).

By this way a chemical reaction between (C) and (A) can be started by which (A) is converted into a polymer-like film-forming substance (E), which is insoluble in (B) and (D). (E) separates at the interface between the continuous and the dispersed phase enveloping every droplet of the dispersed phase (D) with an entirely closed film which represents the capsules.

(A) may also be dissolved in (D) and (C) may be dissolved in (B). In this case the solution of (A) and (D) is dispersed in the solution of (C) in (B).

If (D) is a solid substance (C) is previously absorbed in (D) by suspending (D) in a solution of (C) in water or an organic solvent. The so treated solid is then dispersed in the solution of (A) in (B).

It is also within the scope of this invention to provide more than two film-forming components, if this is necessary for producing the desired film. These components may be located in or on the substance D to be encapsulated or in the dispersion medium in which the capsule formation takes place.

As previously stated, the dispersion medium of the system is preferably water or an organic solvent as, for example, methanol. Under certain conditions, styrene has also proved to be suitable.

Concerning the first film-forming component A, it has been established that metal salts, particularly the alkali metal salts, of alginate, carrageenate and carboxy methylcellulose are particularly suitable. However, cellulose xanthogenate, unsaturated polyester and cellulose ester can also successfully be employed.

If A is in the form of a metal alginate, carboxy methylcellulose or carrageenate, then the component (C) should preferably be a metal salt having a multi-valent cation. Such metal salts are, for example, zinc chloride, ferric chloride, cadmium chloride and calcium bromide. Calcium thiocyanate has also proved to be suitable. Further, it has been found that certain organic acids form suitable films. Thus, it has been established that 5-sulphosalicylic acid forms excellent films upon reaction with sodium alginate.

The substances to be encapsulated may be enriched with additives which do not partake in or are not necessary for the capsule formation. Such additives may, for example, be dyestuffs or pigments.

It will be appreciated that a wide variety of substances and materials may be encapsulated by the inventive method. For example, the material to be encapsulated may be a dyestuff solution or a solution containing a colour reaction component. Various pigments, including magnetic pigments, may be encapsulated by the inventive method. Further, solid compounds having conductive characteristics and substances used for pharmaceutical or chemical purposes may thus be entrapped within the capsule forming film.

The invention will now be described by several Examples, it being understood, however, that these Examples are given by way of illustration and not by way of limitation. All indicated percentages are percent by weight.

EXAMPLE 1.

Substance (D) to be encapsulated: Diphenyloctylphosphate;
medium (B): water;
(A) is sodium alginate;
(C) is zinc chloride.

$$ZnCl_2 + 2\ \text{Na-Alginate} \rightarrow \text{Zn-Alginate} + 2NaCl$$

2 to 10 cc of a 10% solution of anhydrous zinc chloride in diphenyloctylphosphate are dispersed in 100 cc of 0.2 to 2% aqueous solution of sodium alginate. The separating encapsulated droplets are then washed with water.

The droplets of the solution of zinc chloride in diphenyloctylphosphate which are formed by the preparation of the dispersion are coated by an enveloping film of zinc alginate which is insoluble in water.

The washing with water serves two purposes: On the one hand, it removes sodium chloride which is formed during the reaction and on the other hand, it causes the removal of excess zinc chloride within the capsule space by way of diffusion through the alginate film.

EXAMPLE 2.

Substance (D) to be encapsulated: Tributylphosphate;
medium (B): water;
(A) is ammonium alginate;
(C) is ferric chloride.

$$FeCl_3 + 3\ NH_4\text{-Alginate} \rightarrow \text{Fe-Alginate} + 3\ NH_4Cl$$

5—10 cc of a 5—10% ferric chloride solution in tributylphosphate are dispersed in 100 cc of a 0.2—2% aqueous solution of ammonium alginate. The encapsulated droplets are separated and washed with water.

The droplets of the solution of ferric chloride in Tributylphosphate are coated by an enveloping film of Fe alginate which is insoluble in water.

The subsequent washing of the capsules with water serves two purposes: It removes the ammonium chloride which is formed during the reaction and it also causes removal of excess ferric chloride which may be present within the capsule space. This takes place by way of diffusion through the alginate film.

EXAMPLE 3.

Substance (D) to be encapsulated: clay;
medium (B): water;
(A) is sodium alginate;
(C) is cadmium chloride.

$$CdCl_2 + 2\ \text{Na-Alginate} \rightarrow \text{Cd-alginate} + 2\ NaCl$$

10 grams of a finely ground clay are suspended in a solution of 2 grams of cadmium chloride in 100 grams of water at 20°C. After some hours the clay is separated by filtration, washed out with water and dried. 5 grams of the so treated clay were suspended in 100 cc of a 0.1—1% aqueous solution of sodium alginate. The encapsulated clay particles thus formed were separated and subsequently washed with water.

Also in this experiment, the procedure proceeds corresponding to that described in connection with Examples 1 and 2. Each clay particle is encapsulated by a film of cadmium alginate. This film is water insoluble.

EXAMPLE 4.

Substance (D) to be encapsulated: Diethylphthalate;
medium (B): water;
(A) is sodium carboxymethoxycellulose;
(C) is ferric chloride.

5 cc of a 10% solution of anhydrous ferric chloride in diethylphthalate are dispersed in 100 cc of a 0.5% aqueous solution of the sodium salt of carboxymethylcellulose. The encapsulated droplets which separate from the dispersion are washed with water.

EXAMPLE 5.

Substance (D) to be encapsulated: Diphenyloctylphosphate;
medium (B): water;
(A) is sodium carrageenate;
(C) is zinc chloride.

A dispersion is formed by adding 10 cc of a 10% solution of zinc chloride in diphenyloctylphosphate to 100 cc of a 1% aqueous sodium carrageenate solution. The procedure corresponds to that of Example 4 and the capsule droplets are washed with water.

EXAMPLE 6.

Substance (D) to be encapsulated: Tributylphosphate;
medium (B): water;
(A) is sodium carboxymethylcellulose;
(C) is ferric chloride.

A dispersion is formed by dispersion of 5 cc of a 10% solution of ferric chloride in tributylphosphate in 100 cc of a 0.5% aqueous solution of the sodium salt of carboxymethylcellulose. The procedure is otherwise the same as in Examples 4 and 5.

EXAMPLE 7.

Substance (D) to be encapsulated: Trichloroethylphosphate;
medium (B): water;
(A) is sodium carrageenate;
(C) is calcium bromide.

A 10% solution of calcium bromide in chloroethylphosphate is dispersed in 100 cc of of a 1% aqueous sodium carrageenate solution The procedure is otherwise the same as that in the preceding Examples.

EXAMPLE 8

Substance (D) to be encapsulated: Diethylphthalate;
medium (B): water;
(A) is sodium alginate;
(C) is calcium thiocyanate.

5 cc of a 10% solution of calcium thiocyanate in diethylpthalate are dispersed in 100 cc of a 0.2% sodium alginate solution. Otherwise the procedure corresponds to that of the preceding Examples.

EXAMPLE 9.

Substance (D) to be encapsulated: 1% solution of Ceresblue dyestuff in diphenyloctylphosphate;
medium (B): water;
(A) is sodium alginate;
(C) is zinc chloride.

5 cc of a diphenyloctylphosphate solution containing dissolved therein 10% of zinc chloride and 1% of Ceresblue dyestuff are dispersed in 400 cc of a 0.2 to 2% aqueous solution of sodium alginate and in this way, capsules are obtained which envelope a solution of intense blue colour.

EXAMPLE 10.

Substance (D) to be encapsulated: 2% dispersion of soot in diphenyloctylphosphate;
medium (B): water;
(A) is sodium alginate;
(C) is zinc chloride.

3 cc of diphenyloctylphosphate having dis-

solved therein 10% of zinc chloride and containing 2% of suspended gas soot particles are dispersed in 100 cc of a 0.5% aqueous sodium alginate solution. Capsules are obtained which contain a dispersion of gas soot in diphenyloctylphosphate.

EXAMPLE 11.

Substance (D) to be encapsulated:
4% dispersion of graphite powder in benzylbutyladipate;
medium (B): water;
(A) is sodium alginate;
(C) is calcium bromide.

7 cc of benzylbutyladipate containing 5% of dissolved calcium bromide and 4% of dispersed graphite powder are distributed in the form of fine droplets in 100 cc of an aqueous 0.3% sodium alginate solution. The capsules obtained envelope a dispersion of graphite powder in benzylbutyladipate.

EXAMPLE 12.

In the preceding Examples, the component (C) is always a metal salt. The present Example demonstrates that other substances, for example, an acid may serve as component (C), to wit, as component which with a film-forming component (A) yields film compounds which are poorly or completely insoluble.

Substance (D) to be encapsulated;
Diphenyloctylphosphate;
medium (B): water;
(A) is sodium alginate;
(C) is 5-sulpho-salicylic acid.

5 cc of a 7% solution of 5-sulpho-salicylic acid in diphenylphosphate are distributed in very small droplets in 100 cc of a 0.5% aqueous alginate solution. The subsequent processing was performed as in Examples 1 to 6. It will be noted that the medium (B) in Examples 1 to 12 is water or an aqueous solution.

EXAMPLE 13.

In this and the following Example the medium is an organic solvent:
Encapsulated substance (D);
glyceryine; medium (B) styrene;
(A) is unsaturated polyester;
(C) is methylethyl ketone peroxide and cobalt naphthenate.

0.1 gram of cobalt naphthenate were dissolved in 100 grams of "Leguval" (a 70% solution of an unsaturated polyester resin in styrene). "Leguval" is a Trade Mark. The solution was heated to 80°C and 10 grams of glycerine containing 0.4 gram of methylethylketone peroxide were dispersed in the solution under vigorous stirring. Each glycerine droplet is enveloped in this manner with a film of insoluble polyester resin. This Example may also demonstrate that the capsule formation may be caused by the action of more than two components.

EXAMPLE 14.

Substance (D) to be encapsulated:
silicone oil;
medium (B) Methanol;
(A) is Nitrocellulose A 1100
trade designation for a nitrocellulose soluble in alcohols);
(C) is butyl titanate.

5 cc of a 20% solution of butyl titanate are dispersed in 100 cc of a 5% solution of nitrocellulose in methanol. After a few minutes, the silicone oil droplets are enveloped by a cross linked product of nitrocellulose in butyl titanate which is insoluble in methanol.

Dependent on the nature of the substance to be encapsulated, the dispersion degree obtained in the dispersion will vary. Generally, capsules are obtained whose sizes vary between 0.001 to 2 mm.

WHAT WE CLAIM IS:—

1. A method of forming capsules, each capsule comprising an envelope of film material encapsulating a substance, the method comprising preparing a dispersion system by mixing

(D) the substance to be encapsulated,

(B) a liquid dispersion medium, and at least two component (A) and

(C) capable of reacting chemically with each other to form film capsules around particles of the substance to be encapsulated, one of the said components (A) being selected from metal alginate, metal carrageenate, metal carboxymethyl-cellulose, cellulose xanthogenate, unsaturated polyester and cellulose esters and the other component (C) being a low molecular substance selected from metal salts having a multi-valent cation, organic acids, mineral acids, organic peroxides and *o*-titanic acid esters, whereby particles of the substance (D) are encapsulated by the film thus formed.

2. A method as claimed in Claim 1, wherein the substance (D) to be encapsulated is a liquid.

3. A method as claimed in Claim 1, wherein the substance (D) to be encapsulated is a solid.

4. A method as claimed in any preceding claim, wherein the dispersion medium (B) is water.

5. A method as claimed in any one of Claims 1 to 3, wherein the dispersion medium (B) is an organic solvent.

6. A method as claimed in Claim 5, wherein the organic solvent comprises methanol or styrene.

7. A method as claimed in any preceding

claim wherein an alkali metal of the alginate, carrageenate or carboxymethylcellulose is used as component (A).

8. A method as claimed in Claim 7, wherein the alkali metal is sodium.

9. A method as claimed in any preceding claim wherein the said metal salts selected from zinc chloride, ferric chloride, cadmium chloride, calcium thiocyanate and calcium bromide are used as component (C).

10. A method as claimed in any one of Claims 1 to 8, wherein the component (C) is 5-sulpho-salicylic acid.

11. A method as claimed in Claim 1, wherein the sizes of the capsules are between 0.001 and 2 mm.

12. A method as claimed in Claim 1, wherein the said film-forming components are methylethylketone peroxide (C) and unsaturated polyester (A).

13. A method as claimed in any one of Claims 1 to 11, wherein the said film-forming components are butyltitanate (C) and nitrocellulose (A).

14. A method as claimed in any preceding claim substantially as herein described and exemplified.

15. Encapsulated particles when obtained by the method claimed in any preceding claim.

MEWBURN ELLIS & CO.,
Chartered Patent Agents,
70—72, Chancery Lane, London, W.C.2.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.